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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Lined Closures for Containers

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to closures for containers, especially of carbonated beverages, in which the sealing liner includes a particular class of block copolymers combined with special mineral oils.

Containers such as jars and bottles are usually closed by closures comprising a shell, such as a metal or plastic cap, and a sealing liner. In many cases the usual sealing liners have been a disc or ring of cork, although recent developments have been directed to the use of certain thermoplastic materials such as polyvinyl chloride as a cork replacement. On the other hand, the cork is sometimes faced with a disc of aluminium foil, especially in the case of carbonated beverages such as beer. The purpose is to seal the fluid contents within the containers under such conditions that fluid and gaseous components of the contents are prevented from passing through the liner and forming a chemical product with the metal of the closure shell with return of the product back through the liner to the bottle contents and deleterious action thereon both in taste and odour. In such cases, the liner so produced required a cushion between it and the shell to ensure a proper sealing upon the container lip. Hence liners are widely used for container closures and especially so in the case of so-called crown cap closures, wherein the metal cap is crimped against the outside of the bottle opening.

Many of the same problems exist, however, in the closing of containers for non-liquid materials and particularly for such foodstuffs as instant coffee, instant tea and powdered soups. The effort in this case is to preserve the freshness of the food product without imparting any deleterious odour or taste thereto from the sealing material or composition employed for properly closing the container. In the case of many powdered hygroscopic foodstuffs such as instant coffee, the jar at the present time is sealed with a lock closure cap with a waxed paper disc cemented to the rim of the container. Once this disc is opened, however, the contents of the bottle or container thereafter are subject to more or less rapid attack by oxygen with consequent deterioration. Liners of various resinous and rubber compositions have been proposed but tasters have found adverse flavour differences in beer and other beverages so bottled.

According to the present invention, there is provided a closure for containers which comprises a shell adapted for mechanical engagement with the container and extending over the container mouth, and a liner in said shell for engaging and sealing the container lip, the liner comprising a block copolymer having the general configuration

A—B—A

wherein each A is an independently selected polymer block of a monovinylarene, each A block having an average molecular weight between 18,000 and 35,000, and B is a polymer block of a conjugated diene, the block having an average molecular weight between 35,000 and 70,000 and hydrogenated derivatives thereof; and 20 by 100 parts by weight of a mineral oil extender per 100 parts by weight of block copolymer.

An illustrative cap is shown in the accompanying drawing wherein Figure 1 is a perspective view of a typical closure containing a liner and Figure 2 is an axial diametric section.

In these drawings, the crown shell 10 is shown with a domed central portion 11 merging into a curved portion 12 known as the top corner radius. While it is not necessary in all cases, the edge of the shell may be provided with a corrugated skirt above the outer margin of the top corner radius, with alternate ribs 13 and grooves 14, the ribs having portions 15 with a small upward and outward slope as shown in Figure 2. This is a known conformation shown illustratively and permits crimping upon the container neck. The liner 20 is of optional shape and thickness insofar as the present invention is concerned but may have a central circular portion 21 and preferably but not necessarily has integral therewith a thicker angular portion 22 which may be formed as a plurality of concentric ribs. Due to the special nature of the compositions of the liner as described herein, however, the ribs are not an essential feature of these structures. The lower face of the liner in Figure 2 is adherent to a portions 11 and 12 of the shell and the liner may but preferably does not extend above the lower ends of the grooves 14 as shown in Figure 2.

The block copolymers forming the essential component of the present liner composition have the general configuration A — B — A and may be either hydrogenated or utilized without hydrogenation. Prior to hydrogenation, the blocks A comprise non-elastomeric blocks of the group consisting of monovinyl arene polymer blocks while the centre blocks B are polymer blocks of conjugated diene, preferably having from 4 to 8 carbon atoms per molecule. The essential feature other than the structure is in regard to the molecular weight ranges permissible for the provision of odour and taste free container liner compositions. For this specific reason, it has been found necessary to employ block copolymers in which each block A has an average molecular weight from 18,000 to 35,000 and block B has an average molecular weight of 35,000 to 70,000. Typical block polymers of this type are those having the general configuration polystyrene-polyisoprene-polystyrene or polystyrene-polybutadiene-polystyrene.

For special purposes it may be desirable that the block copolymer be subjected to hydrogenation. This may be of any desired degree and preferably comprises hydrogenation of at least about 50% of any double bonds existing in the diene portion of the block copolymer.

The block copolymers are to be used in conjunction with mineral oils of a particular class chosen to minimize or completely eliminate odour or taste problems, especially if the containers are contemplated for use in food marketing and storage and particularly in the case of beverages such as carbonated drinks and particularly beer. For this purpose it is necessary to employ a mineral oil having a minimum aromatic content and preferably treated in such a way as to remove any deleterious polar compounds or colour bodies. Optimum for this purpose is medicinal white oil, but paraffinic or naphthenic or mineral oils may be employed, the oils having from 0—25% by weight of aromatic hydrocarbon content. Preferred oils have a viscosity at 100°F of 200—500 SSU and a viscosity at 210°F of 40—65 SSU. They should have pour points between about −50 and +10°F and have viscosity-gravity constants between about 0.8 and 0.9 In order to provide the processability and modulus desired for the particular end use in mind, it is necessary to utilize between 20—100 parts by weight of oil per 100 parts of block copolymer. This ratio will be referred to herein as "phr". Preferably, the amount of oil is between about 40—60 phr, while optimum processing and other aspects are obtained when the amount of oil is between about 45 and 55 phr.

In the first place, it can be said that any of the block polymers of the configuration stated hereinbefore might be employed for the preparation of container cap liners if equipment considerations, processability, clarity, odour and taste could be ignored. However, these are very real commercial limitations which must be met if the product is to be commercially acceptable. For example, block copolymers having the same general configuration but having molecular weights outside of the ranges given hereinabove can be formulated to be suitable for use in the presently employed bottle cap lining equipment; however, in order to do so, the latter polymers must be modified with low molecular weight resins and other additives in order to impart the correct modulus and hot melt characteristics for their use in the subject equipment. When such modifications are formed, however, and lined it has been found that they develop objectionable odour or taste problems. This is especially critical in such areas as commercial beer bottle closures where extremely rigid standards of odour and taste are maintained in order to prepare a constant high quality product for public consumption which does not involve objectionable odour or taste.

In addition to the crown cap liners such as utilized for illustrative purposes in the appended figures, the lining compositions of the present invention may be employed in the lining of other container closures. These include tear-off or tab tops which require a ring of lining material for sealing. Another recent development in the field of bottle closures is in a twist-off cap especially designed for large size carbonated beverage bottles which may be opened by untwisting the cap from the neck of the bottle and after partial use the bottle can be closed by twisting the cap back on. One of the problems here is in proper sealing of the neck of the bottle with this cap during its use. The present sealing compositions pro-

vide an effective sealing line for this type of closure and perform this function without failure and without imparting any objectionable odour or taste to the enclosed product.

Still another type of closure to be used in conjunction wuth the subject liners is for wider mouthed containers used, for example, in the marketing of instant coffee to replace the wax paper seals which are found to be only temporary at best and of no use once the seal has been cut. This type of closure is normally a lock or bayonet type of wider diameter than utilized for ordinary beverage bottle containers. In this case, the liner may perform its sealing function as a ring in the suitable part of the cap, thus contacting the rim of the jar or other containers such as a "tin" without the entire surface of the cap so lined. Of course, it is also possible to line the entire cap. While these coatings have been found to be tightly adherent to the lacquered metal normally employed for crown cap construction, it is also possible to use the compositions for the surface coating of cork liners or the like or even for the surface coating or lamination with polyvinyl chloride types of liners. It is, moreover, possible to construct the bottle closure in such a way that the liner and cap are made of the same material and, in fact, are a single unit rather than a composite structure. In this case the entire closure, i.e., cap and seal either separate or as one piece are formed of the block copolymer. This permits facility in opening and closing containers and at the same time obtaining the high degree of sealing which is necessary for proper storage and preservation of the contents of the containers. The caps in this case may be extended with a tab for using a thumb and finger to facilitate lifting of the cap from the container.

There are three generally employed methods for producing plastics crown cap liners used in the industry today: these include moulded in place, flowed-in and a combination foam-moulded method. Recently an improved method has been developed which employs a machine for moulding a plastics material directly into the interior surface of the crown caps, thus combining the moulding and assembly into a one-step operation. In this method, polymer pellets are fed to the hopper of an extruder where they are melted and fed into the head of the lining section. The hot polymer is deposited into the crown cap shells which have been preheated in a furnace. Water-cooled dies then mould the polymer into the liner configuration and discharge finished crowns. The process possesses several advantages over the flowed-in method employing a polyvinyl chloride plastisol in that it avoids batch variations and plastisol spillage. The plastisol flowed-in method, moreover, requires injection of the plastisol into a rotating crown, requiring a relatively costly piece of equipment for this operation. The moulded in place technique, also requires baking in an oven to remove solvent or low boiling plasticizer from the formulation. The present invention provides an improved composition which particularly contemplates the type of operation wherein a hot liner composition is directly moulded into the inner surface of the crowns. This does not exclude, however, the formation of sheet, the cutting of liner discs and this adherence to the inner surfaces of crown caps or other closures, especially when rings or other seal configurations are required.

It was found that the optimum composition for this purpose had the structure polystyrene-polybutadiene-polystyrene and had average block molecular weights of 23,000 — 45,000 — 23,000 as determined by intrinsic viscosity measurements, as they are related to osmotic molecular weights. This particular resin could be suitably extended by the use of two types of mineral oil, a medicinal white oil on the one hand having virtually no aromatic content and a refined naphthenic oil on the other hand having an aromatic content in the order of about 15% by weight. Both of these oils are non-toxic and can be utilized in contact with food products. The medicinal white oil has certain advantages in its lack of colour, thus producing a virtually colourless liner composition in conjunction with the colourless polymer.

Example

Formulations containing 50 parts by weight of oil and 100 parts by weight of a block copolymer were mill mixed and either extruded for the formation of chopped nibs or slot cast into film approximately 0.013—0.016 inches gauge. The block copolymer used had the structure polystyrene-polybutadiene-polystyrene and had average block molecular weights of 23,000 — 45,000 — 23,000. Sample A contained a refined naphthenic petroleum oil, while Sample B contained a medicinal white oil. The extrusion conditions during nibbing and slot casting are given in the following table:

TABLE I

Extrusion Conditions

Sample	A	B
Extruder/Nibber		
Condition		
Barrel Temperature, °C. (max.)	150	150
Die Temperature, °C.	160	170
Screw Speed, rpm.	60	60
Extruder — Slot Film Casting		
Condition		
Barrel Temperature, °C. (max.)		
Zone 1	162	163.5
Zone 2	162	163.5
Die Temperature, °C.	190	190
Screw Speed, rpm.	76	42
Film Thickness, cm.	.356	.381
Film Transparency	Clear	Clear

Both of the formulations extruded into strands satisfactorily at the temperatures used and caused no odour problems. In comparison, nibs and sheet were prepared using a block copolymer polystyrene-polybutadiene-polystyrene having average block molecular weights of 14,000 — 53,000 — 14,000. It was found necessary to incorporate a substantial amount of alpha-methyl styrene in order to achieve the desired processability for commerciallly available equipment and at the same time to obtain the desired hardness, modulus, clarity and resilience. These nibs and sheets were judged by an odour panel to have a strong and objectionable odour.

In order to examine the the sealing properties of the new compositions, liners were cut from samples of slot cast film, cemented into metal crowns with a small amount of the same composition dissolved in toluene and used to test sealed samples of water and beer. The method used in the trade for testing sealing properties, in which bottles of water are stored in an inverted position at 180°F for one hour, was used. In addition, a more severe test using inverted bottles of beer stored at 180°F for up to 8 hours was also carried out. The results of the seal test given in the following table proved the acceptability of the sealing compositions.

TABLE II

Sealing Tests

Time (Hour)	Beer Tests at 180° F.	
	Sample A	Sample B
1	No leak detected	No leak
2	No leak detected	No leak
4	No leak detected	No leak
8	No leak detected	No leak

WHAT WE CLAIM IS:—

1. A closure for containers which comprises a shell adapted for mechanical engagement with the container and extending over the container mouth, and a liner in said shell for engaging and sealing the container lip, the liner comprising a block copolymer having the general configuration

A—B—A

wherein each A is an independently selected polymer block of a monovinyl arene, each block having an average molecular weight between 18,000 and 35,000, and B is a polymer block of a conjugated diene, the block having an average molecular weight between 35,000 and 70,000, and hydrogenated derivatives thereof; and 20 to 100 parts by weight of a mineral oil extender per 100 parts by weight of block copolymer.

2. A closure according to claim 1, in which in the block copolymer the A blocks are polystyrene.

3. A closure according to claim 1, in which in the block copolymer, the B blocks are polybutadiene or polyisoprene.

4. A closure according to any one of the preceding claims, in which the mineral oil is a medicinal white oil.

5. A closure according to any one of the preceding claims, in which the mineral oil is a naphthenic petroleum oil having less than 25% by weight of aromatic hydrocarbon content.

6. A closure according to any one of the preceding claims, in which the amount of mineral oil is between 40 and 60 phr.

7. A closure according to any one of the preceding claims, wherein the closure is a crown cap.

8. Containers closed by the closures claimed in any one of claims 1 to 7.

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1125499 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

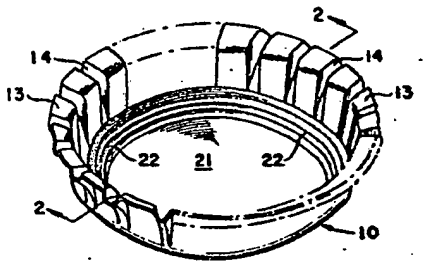

FIG. 1

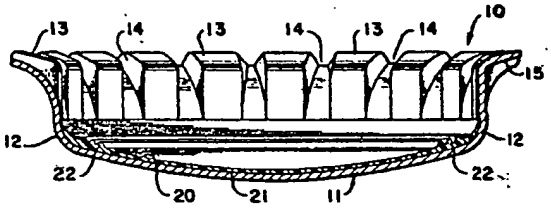

FIG. 2